

Book Reviews *

Salt Effects in Organic and Organometallic Chemistry. By A. Lopy and B. Tchoubar (CNRS). VCH: Weinheim, New York, Cambridge, Basel. 1992. xvi + 315 pp. \$125.00. ISBN 0-89573-954-2.

This nine-chapter book is a translation of the French edition published in mid-1988 by Dunod (Paris). In this translation, parts of the French version have been further elaborated, revised, and augmented with improved style for easier reading. According to the preface, this book does not intend to cover all publications involving the influence of salts on chemical reactions, but rather, to develop a general knowledge and a qualitative understanding of the causes of the various salt effects in organic and organometallic chemistry. Throughout the book, the authors have focused on the general principles to explain salt effects in a number of reactions and they have given some selected examples to illustrate them. Due to the time lag between the publication of the original version and the translation, this book should not be viewed as a literature survey but rather as a textbook that defines and illustrates some general guidelines and principles of salt effects.

The first chapter defines and illustrates these five general types of salt effects: (a) involving the salt's Lewis acid or base character; (b) arising from exchange reactions between two ion pairs; (c) connecting with the position of ionic dissociation equilibrium; (d) affecting the structure of the activated complex in the transition state; and (e) arising from specific associations with protic solvents.

Chapter Two reviews the effect of salts on the rates of single bond cleavage reactions. More specifically, salt effects in the unimolecular and bimolecular substitution and elimination reactions are discussed from a kinetic point of view as well as in C-H bond ionization.

Chapter Three reviews the effect of salts on the rates of addition reactions to multiple bonds. The general principles of positive and negative salt effects on the rate of addition to carbonyl groups, nitriles, and carbon-carbon double bonds are presented, and selected examples are discussed. Basic principles of double activation using bifunctional catalysis, such as the use of the LiBr/Et₃N couple in the Horner-Emmons reactions, are also briefly explained.

The macrocycle synthesis via the kinetic or the thermodynamic template effect is the subject of the beginning of Chapter Four. The effect of salts in a number of other reactions, in which the regioselectivity is an issue (epoxide opening, 1,2- vs 1,4-addition to α,β -unsaturated carbonyl compounds), is surveyed. The chapter ends with a discussion of the effects of salts on the nature and distribution of electrophilic addition reaction products.

Chapter Five, which discusses the effects of salts on reaction stereochemistry, is by far the largest chapter in this book. The effects of salts on carbonyl addition reactions (reduction, organolithium, aldol condensation, and Wittig reaction) are reviewed again, and selected examples are provided. A whole section of this chapter is devoted to asymmetric synthesis and to the Favorskii Rearrangement. Finally, a discussion of the stereochemistry of enolate protonation concludes this chapter.

Chapter Six illustrates the specific effects of salts on equilibrium preceding the slow step of various reactions and on equilibrium between ion pairs.

The last chapter (Chapter Seven) is divided into two parts. The first is devoted to the organic compounds of some main group metals, and the second concerns organotransition metal compounds. After an initial discussion of the structural features of alkylolithiums and Grignard reagents (with and without salts), some of their reactions in the presence of salts are briefly discussed. The last thirty pages of the chapter are devoted to salt effects in transition metal chemistry. Salt effects in some selected reactions (Heck type cross-coupling reactions, organocuprate additions, Wacker oxidation) are discussed in more detail.

The book ends with an Appendix that reviews some general concepts used in this book. One has to wonder whether this section is really useful, since this book is targeted at advanced chemistry students and practicing chemists with strong backgrounds in organic and organometallic chemistry.

Since this book is a translation, most of the literature citations (over 1300) are pre-1988. To partially circumvent that problem, the authors have also included a list of about 50 additional recent references (1988-1989) that includes both the title of the publication and in which section of the book the publication should have been discussed.

This book contains a wealth of information in several areas of organic and organometallic chemistry which makes the text extremely concise. The authors have been able to gather a large number of literature examples

on a topic that has not been reviewed recently. They have tried to qualitatively explain many experimental results involving salt effects in organic chemistry. It remains to be seen, however, how valid these explanations are. The drawings and the overall presentation is generally acceptable. Perhaps the section of Chapter Five on salt effects in asymmetric synthesis is somewhat weak if one takes into account all the progress that has been achieved in this area over the last 10 years. Furthermore, a reclassification of this book by reaction type (carbonyl addition reaction, enolate formation, substitution reaction, etc.) rather than by the general aspects of reactivity (regioselectivity, reaction rates, stereochemistry) might have prevented some repetition and made the reading easier (for example, discussion of carbonyl addition reactions can be found in five chapters!).

In summary, this book on the various salt effects in organic and organometallic chemistry will be a useful addition to libraries and should help researchers to solve general problems in organic chemistry.

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Chromatographic and Electrophoretic Methods. By Thomas J. Bruno (NIST). Prentice Hall: New York. 1991. xvi + 216 pp. \$58.00. ISBN 0-13-806811-9.

In the introduction, the author explains that this book is intended to provide an introduction to chemical instrumentation for nonchemists. It appears to me that he is successful in this endeavor. The text is very descriptive, with a minimal amount of theory. The book consists of five chapters and covers gas, liquid, and supercritical fluid chromatography and electrophoresis. No technique is covered thoroughly, but each is explained in enough depth for a lay person to understand the principles of its operation. This is not a book for experienced scientists, because it contains some very basic chemistry. For example, the first chapter is devoted to "the nature of mixtures", and is a concise description of the chemical and physical properties commonly exploited in separation science. In the chapter on electrophoresis, the chemical structures of amino acids, proteins, and nucleotides are described. The author also provides a glossary at the end of the book for quick reference to terms which may be new to the reader.

The chapter on gas chromatography discusses the use of gas-liquid, gas-solid, and capillary-based separations. Problems with sample introduction are discussed. Most of the currently available detectors (including mass selective detectors) are explained in detail, along with the types of compounds for which they are useful. The next chapter, on liquid chromatography, describes liquid-liquid, ion-exchange, and size-exclusion chromatography. Ion-pair chromatography is not explained, although it is mentioned in one of the tables. There is no discussion of preparative chromatography in this chapter, although one would assume that this would be of interest to nonchemists working in industrial settings. The description of detectors here is much less thorough than that for gas chromatography. Fluorescence and electrochemical detectors are barely mentioned; however, UV and refractive index detectors are described in detail.

The chapter on supercritical fluid chromatography examines the advantages and disadvantages of the technique, including the unique instrumental requirements. This chapter includes a description of what types of mobile phases and stationary phases can be employed in SFC. The last chapter is devoted to electrophoresis. It deals strictly with conventional gel electrophoresis with no mention of the increasingly popular capillary electrophoretic techniques. The use of polyacrylamide gels (PAGE) for the separation of polynucleotides is discussed, but there is no mention of SDS-PAGE, which is one of the more important methods of protein separation.

Finally, there is an appendix at the end of the book which discusses methods of calibration. This is an important addition to the book, since many nonchemists do not understand how analytical data are obtained. This chapter explains the possible methods of instrument calibration and the advantages and disadvantages of each.

In summary, this is a good book for a nonchemist who interacts with analytical chemists on a daily basis. It does a good job of explaining the instrumentation commonly employed for analytical separations. In addition, the author informs the reader about which techniques are appropriate for which types of problems and the order of complexity of the techniques. The chapter on calibration explains in simple terms how

*Unsigned book reviews are by the Book Review Editor.

quantitative results are obtained, and the glossary provides an easy way for the nonchemist to look up terms which may be unfamiliar to him or her.

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Applied Many-Body Methods in Spectroscopy and Electronic Structure. Edited by Debashis Mukherjee. Plenum Press: New York. 1992. viii + 292 pp. \$79.50. ISBN 0-306-44193-4.

This book contains the proceedings of a symposium on the title subject held in Calcutta, India, December 10–12, 1990. There are 10 chapters, a list of contributors, and a brief subject index.

Thermodynamic Properties of Isomerization Reactions. By M. L. Frenkel (Texas A&M University), G. Ya Kabo (Byelorussian State University), and G. N. Raganov (Mogilev Institute of Technology). Hemisphere Publishing Corporation: Washington. 1992. viii + 230 pp. \$85.00. ISBN 1-56032-111-3.

This book represents a valuable compilation of thermodynamic values (ΔH) for a large number of isomerization reactions. After a brief introduction of 15 pages detailing some of the methods for obtaining this information as well as the problems associated with different techniques, the book continues with almost 200 pages of tables of ΔH and ΔS values for isomerization reactions. The compounds are listed sequentially by formula, and the temperature of the experiment as well as the technique and literature reference is provided.

Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice. By J. P. Kennedy and B. Ivan (University of Akron). Oxford University Press. New York. 1992. xvi + 240 pp. \$88.00. ISBN 0-19-520921-4.

Two decades ago, all the textbooks of polymer chemistry were focusing on anionic processes and their potentialities in tailoring macromolecules. The parallel cationic mechanism was largely disregarded. Just ten years ago, Kennedy and Marechal published a comprehensive survey of cationic polymerization. Although the molecular design of polymers by this technique was next to impossible at that time, the authors claimed that a quiet revolution in the field was beginning to take place. Today this book by Kennedy and Ivan devoted to the carbocationic macromolecular engineering proves that the revolution was more sweeping than even an optimist would have expected.

Anyone reading this book will find the first comprehensive overview of the large amount of information that has appeared during the past two decades in the scientific and patent literature. It is a pleasure to read how all the elementary steps—initiation, propagation, transfer, and termination—have fallen under the control of the polymer chemist and how all the available data have been condensed into interlocking concepts which are invaluable guides for the synthesis-oriented industrial and academic chemists.

As announced in the title, the book is subdivided into two large sections: theory and practice. The theoretical part deals with the basic methodologies on which carbocationic macromolecular engineering is founded. A general up-to-date introduction to carbocationic polymerizations is followed with cationic polymerization fundamentals and mechanisms. The practical part concerns specific products that have already been prepared as a result of carbocationic macromolecular engineering. Special attention is devoted to telechelics and their uses, block copolymers, graft copolymers, and networks. Some considerations on emerging technologies and a glimpse into the future close this timely publication, which comes from acknowledged experts in the field.

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Molecular Recognition: Chemical and Biochemical Problems II. Edited by Stanley M. Roberts (University of Exeter). Royal Society of Chemistry. Cambridge, U.K. 1992. viii + 200 pp. £39.50. ISBN 0-85186-226-8.

This book was developed from a symposium sponsored by the Fine Chemicals and Medicinal Group of the Industrial Division of the Royal Society of Chemistry held in Exeter on April 6–10, 1992. After a preface by the editor, the book contains 16 chapters. There is a short subject index.

Luminescence Techniques in Chemical and Biochemical Analysis. Edited by Willy R. G. Baeyens and Denis DeKeukeleire (State University of Ghent) and Katherine Korkidis (Spex Industries). Marcel Dekker. New York, Basel, and Hong Kong. 1991. xv + 654 pp. \$150.00. ISBN 0-8247-8369-7.

The book is composed of nineteen chapters by different authors. Topics include an overview of luminescence analysis and fluorescence, theory and instrumentation in pulsed and frequency domain fluorimetry, fluorogenic reagents and probes, circular polarized luminescence, fluorescence line narrowing, laser based detection in liquid chromatography, luminescence techniques for studying polycyclic carcinogen–nucleic acid interactions, fluoroimmunoassay, multidimensional luminescence spectroscopy, and fluorescence-detected circular dichroism. There is also a chapter on sample clean up in liquid chromatography, which is potentially useful but has no luminescence component. There are several chapters on chemiluminescence (CL) analysis, design and synthesis of chemiluminescence reagents, CL in flowing streams such as FIA and HPLC, 1,2-dioxetane chemistry and applications, and enhanced horseradish peroxidase CL in ligand analysis. Most of the articles are of a review nature and frequently highlight the authors' work. The primary emphasis is on biochemical analysis, although many of the topics are of a much broader interest.

The writing is generally of good quality, the topics of general interest, and the level such that one not intimately familiar with an area can learn the basics and where to go for further details. The format in such areas as references is not always consistent, and some of the authors appeared unaware of related chapters in the book, which led to some duplication of effort and a less efficient presentation. For example, Chapters 8 and 10 are devoted almost exclusively to interactions of polycyclic carcinogens with DNA, yet the two do not seem to recognize the existence of the other. An unfortunate weakness of the review component is that there are virtually no references beyond 1988 with several having none later than 1987; this is unsatisfactory for a book with a 1991 copyright.

Who will find this book valuable? Specialists in a given area will probably find the articles in their specialty of marginal value, especially given the lack of recent references. People who will find it of most use are those not intimately familiar with a given area. In particular, the range of topics is interesting and spans many that may not be immediately familiar to the average reader. This book provides an introduction to, and the potential applications of, a variety of these techniques. It is, thus, likely to spawn new research ideas and methods for attacking existing problems. The book is not generally suitable for instructional use because of the review character and the brevity of many of the chapters. An exception is Laser Based Detection in LC, where the authors give a good overview of experimental luminescence methods including a survey of laser light sources. While many are likely to find a number of articles useful and thought provoking, the high price will largely limit its distribution to libraries.

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Organic Reaction Mechanisms, 1990. Edited by A. C. Kripe and W. E. Watts (University of Ulster, Northern Ireland). John Wiley & Sons. Chichester, England. 1992. ix + 654 pp. \$350.00. ISBN 0-471-93103-9.

This volume is the twenty-sixth in an annual survey of the literature on organic reaction mechanisms. It covers the period December 1989 through November 1990. Given the number of papers published each year on reaction mechanisms, the desire that the survey should be comprehensive, and the need to keep the volume to a manageable size, only a one or two sentence capsule summary is given for each paper; yet, by grouping papers on related topics together in a skillful way, the editors and their contributing authors manage to provide a volume that is also quite readable.

Keeping up with the voluminous literature of organic reaction mechanisms is a real challenge for those working in the field. There is always concern about overlooking a paper that has significant importance for some of one's current research. A comprehensive, well-done annual survey such as *Organic Reaction Mechanisms* prevents this from happening and is therefore a real godsend.

While this survey covers the majority of research in organic reaction mechanisms in a series of fifteen chapters dealing separately with different types of reactions (e.g., radical reactions, nucleophilic aliphatic substitution, elimination reactions, molecular rearrangements, etc.) and different kinds of reactive intermediates (e.g. carbenes and nitrenes, carbocations, carbanions, etc.), it does not attempt to cover those areas (such as photochemical reactions, organometallic chemistry, heterogeneous catalysis) that are currently treated by other specialized reviews.

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